

The University of Chicago

I. RESISTANCE THERMOMETRY. II. AN EXPERIMENTAL INVESTIGATION OF THE POSSIBILITY OF USING ALTERNATING CURRENT TECHNIQUE IN THE MEASUREMENT OF SMALL TEMPERATURE DIFFERENCES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1941

By
WARREN ELLIOTT HENRY

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ACKNOWLEDGMENT

The writer expresses appreciation to Professor T. F. Young for his friendly advice and counsel which made this investigation possible. Thanks go also to Mr. Persa Raymond Bell for technical advice in the construction of apparatus.



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PART I

RESISTANCE THERMOMETRY

Since energy relations are frequently measured by temperatures and temperature differences, precision measurements of these quantities are indispensable for the solution of many thermodynamic problems. In particular, methods of measuring small temperature changes in dilute solutions have found widespread application.¹ The most sensitive instrument yet found for carrying out such measurements is the thermel.² However, in the hope of finding a technique more suitable for certain purposes than the thermoelectric method, Galen W. Ewing³ surveyed the possible means of measuring small temperature differences. Those which he thought sufficiently sensitive were the methods depending on the temperature coefficients of (1) dielectric constant, (2) resistance, (3) electromotive force of cells, and possibly (4) magnetic permeability. Of these, he considered the first two the most promising and studied the dielectric constant method. He investigated especially the use of Rochelle salt crystals as the dielectric of a condenser. The second method (the resistance method) is the subject of the study described here.

History of the Resistance Thermometer

Resistance thermometry was probably foreshadowed by the

¹Merle Randall and Frederick D. Rossini, J. Am. Chem. Soc., **51**, 323 (1929); E. Lange and A. L. Robinson, Chem. Rev., **9**, 89 (1931); T. F. Young and W. L. Groenier, J. Am. Chem. Soc., **58**, 187 (1936); T. F. Young and J. S. Machin, J. Am. Chem. Soc., **58**, 2254 (1936); T. F. Young and Paul Seligmann, J. Am. Chem. Soc., **60**, 2379 (1938); Frank T. Gucker, Jr., Hugh B. Pickard, and Ralph W. Planck, J. Am. Chem. Soc., **61**, 459 (1939); Curtis R. Singleterry, Ph. D. Dissertation, University of Chicago, 1940.

²E. Lange and A. L. Robinson, op. cit.; Frank T. Gucker, Jr., Hugh B. Pickard, and Ralph W. Planck, op. cit.; Robert H. Ralston, Ph. D. Dissertation, University of Chicago, 1940.

³Galen W. Ewing, Ph. D. Dissertation, University of Chicago, 1939.

observation by Becquerel⁴ of a qualitative relation between resistance and temperature. When a glass tube was charged inside and then hermetically sealed, he found that so long as the temperature was not raised, no electric effects could be noted externally. But when the tube was heated, the electric charge began to manifest itself outside, thus indicating an increased conductivity of the glass. Prompted by this phenomenon, Becquerel investigated the temperature coefficients of conductivity of certain metals. Other workers⁵ followed up these first crude measurements. Various formulas for the temperature dependence of resistance were suggested⁶ and by about 1860 the methods of temperature measurement had been so much refined that it was possible to detect temperature differences of 0.1°C .

When the technique had reached this degree of precision, a formula, based on theoretical considerations, for the relation between temperature and resistance became highly desirable. Probably the first such formula is that of Siemens.⁷ It is based on a mechanical model and on the assumption that the electrical resistance of a metal is directly proportional to (1) "the velocity of the atomic vibrations which constitute the thermal energy of the metal" and (2) the distance between the atoms of the metal. The first factor leads to a term in $T^{1/2}$ since T is proportional to v^2 . The second factor leads to a term in T with a proportionality coefficient dependent on the temperature coefficient of expansion of the metal. Siemens' final formula is

$$R = AT^{1/2} + BT + C$$

The resistance of platinum was found to follow this parabolic law moderately well. Encouraged by these results Siemens conceived the idea of using resistance as a means of temperature measurement, and by the construction of an instrument laid the foundation for resistance thermometry. The advantage of Siemens' method was that

⁴M. Becquerel, Memoires de l'Academie de Science, 11, 317 (1832).

⁵W. Thompson, Phil. Mag., 551 (1851); M. Lamy, Comptes rend., 43, 693 (1856); J. Muller, Pogg. Ann., 103, 176 (1858); Augustus Matthiessen and M. von Bose, Phil. Trans., 152, 1 (1862).

⁶R. Clausius, Pogg. Ann., 104, 650 (1858).

⁷C. W. Siemens, Proc. Roy. Soc. London, 19, 351 (1871).

it could be used for the measurement of temperature in inaccessible or distant places such as the interior of furnaces or underground regions. In applying this method to the determination of temperatures between 0° and 100°C. , two equal resistances were used in a bridge. One was placed in the region of unknown temperature, the other in a water bath. The temperature of the bath was adjusted until no current flowed and then measured with a mercury thermometer. The temperature thus obtained was taken as that of the region of unknown temperature. The application of this method required no assumption of any definite relationship between resistance and temperature.

Another method of measuring the temperature by means of resistance is to use equal coulometers connected in parallel. One of these is in series with a known stable resistance; the other with the resistance whose temperature is to vary. From the volume of gas liberated in each coulometer during an arbitrary time interval the resistance is calculated as follows: Since the potential E , applied to both sets of resistances is the same,

$$E_1 = E_2$$

and hence

$$R_1 I_1 = R_2 I_2$$

The volume, V , of gas liberated is proportional to the current, I . Therefore

$$R_1 V_1 = R_2 V_2$$

$$R_1 = X + \gamma_1$$

where X is the variable resistance and γ_1 the resistance of the coulometer in series with it.

$$R_2 = C + \gamma_2$$

where C is the fixed resistance and γ_2 the resistance of the second coulometer. Where $\gamma_1 = \gamma_2$

$$(X + \gamma) V_1 = (C + \gamma) V_2$$

$$X = \frac{V_2}{V_1} (C + \gamma) - \gamma$$

Errors due to differences in the lengths of the leads are eliminated by a third wire connecting the bridge to the resistance

coil. This method gave values for resistance within 0.5 per cent of those obtained by the Wheatstone bridge method. Siemens discovered that impurities such as iridium made his platinum resistances unreliable. By using pure wire, a constant temperature oil bath, and a Wheatstone bridge, he obtained results reproducible up to 350°C . Thus he determined resistance-temperature formulas for platinum, copper, iron, aluminum, and silver.

When Siemens announced his invention of a platinum resistance thermometer, the British Association appointed a committee to investigate it. This committee reported changes in resistance when the resistance element was heated and then brought back to its initial temperature. The committee also criticized Siemens' calibration of his thermometer. At lower temperatures, he had used an unstudied mercury thermometer and at high temperatures a calorimeter. He had assumed the specific heats of water and copper balls to be independent of temperature and had neglected heat losses during the transfer of the copper balls to the water. This report aroused a scepticism regarding resistance thermometry which retarded its normal development for a generation.

Modern precision resistance thermometry was developed mainly by H. L. Callendar⁸ who enunciated the rules and criteria necessary for precise and reliable temperature measurements. He realized that the requirements were (1) easily measurable resistances with large temperature coefficients of resistance, so enclosed that they quickly come to thermal equilibrium with the material the temperature of which is to be measured; (2) a dependable, accurate method for measuring resistance; (3) an accurately known relationship between the resistance of the resistance unit and its temperature; and (4) accurately reproducible fixed points at which to convert the resistances into temperatures on the gas scale. So nearly did Callendar realize these conditions that in forty years his resistance method of measuring temperatures and temperature differences has been but little improved.

The necessary qualifications for a good metal resistance unit are set forth by Callendar⁹ as follows: (1) the resistance should be constant at a given temperature and independent of the

⁸H. L. Callendar, Phil. Trans., 178, 160 (1887).

⁹Ibid.

history of the unit; (2) the unit should be easily and accurately reproducible as well as portable; (3) the metal resistance temperatures should agree with accepted standards; and (4) the resistance unit should be applicable to varied types of investigation.

Callendar compared his resistance thermometer with the air thermometer, since the thermodynamic scale was not at that time available. He consequently encountered several difficulties with the air thermometer such as the thermal expansion of the glass bulb and the adsorption of the air on the glass. For the first of these a correction was introduced. There was also an increase in the volume of the bulb due to increase in air pressure, especially near the softening point of the glass; this difficulty was avoided by adjustment of the air pressure so that when the bulb reached the high temperature the internal pressure was one atmosphere. To insure that the platinum resistance element was in temperature equilibrium with the air in the thermometer, this element was enclosed in the air bulb.

Callendar's resistance measurements were made with a Wheatstone bridge and a Thompson mirror galvanometer used as a balance indicator. The battery consisted of six Le Clanché elements. Since the resistance (500 ohms) in the circuit was large, the current was allowed to flow continuously. With this arrangement, it was possible to measure resistance to 1 part in 10^5 . Two corrections were necessary: One amounting to 0.016°C . for the heating effect of the 0.1 ampere current and another for the temperature coefficient of resistance of the bridge units. Thermoelectric effects made the galvanometer unstable. The observations were in error by as much as 2° at 250°C .

Callendar found that the temperatures determined by his method differed slightly from those determined by gas thermometry. The differences may be expressed by the formula

$$t_g - t_p = 1.57 [(t_g/100)^2 - (t_g/100)]$$

where t_g and t_p are respectively the temperatures on the gas and platinum scales. This equation is equivalent to

$$R_{t_g}/R_0 = 1 + \alpha t_g + \beta t_g^2$$

where R_{t_g} and R_0 are respectively the resistances at t_g and the freezing point of water. Although these formulas are not entirely satisfactory, Callendar's thermometer was successfully used in

the measurement of steam pressures. Benoit and Matthiessen used exponential formulas which were satisfactory over short temperature ranges.

In 1891, Callendar¹⁰ further improved the platinum resistance thermometer and showed that if the platinum element was annealed and free from strain and impurities, it was superior to the other types of thermometers because of the stability of its zero point. This result was not at first believed because of the unfavorable British Association report on the Siemens thermometer. Callendar showed, however, that the wire in Siemens' instrument was wound on clay which attacked platinum; furthermore this wire, because of the temperature gradient in it, was under strain and showed cracks visible through a microscope.

An idea of the advantage of the resistance thermometer over the mercury thermometer at this point in its development may be obtained from the following facts. The range of the platinum resistance thermometer was from -208° to 1770°C . whereas that of the mercury thermometer was -40° to 400°C . When the platinum resistance element was heated for a week at 350°C . the readings scarcely changed whereas the readings on the mercury thermometer showed changes of 10-20 degrees. The accuracy of the mercury thermometer was only 0.1° at 200°C . while the accuracy of the platinum thermometer was 0.01° up to 500°C . A very accurate method for calibrating the resistance element was developed by Griffiths.¹¹ He used three fixed points: the ice point at 0°C ., the steam point at 100°C . and the sulfur boiling point at 444.7°C . The platinum resistance thermometer thus calibrated was found accurate within 0.004° , and when special care was exercised, within 0.001° , at 50°C . In 1894 Cary Foster therefore published in Nature a letter stating that the findings of the British Association's committee with regard to the Siemens thermometer did not apply to resistance thermometers in general. This letter was the first step towards the abandonment of the taboo which had hitherto suppressed the development of this new method of temperature measurement. When the reliability of the resistance method was thus

¹⁰H. L. Callendar, Phil. Mag., **32**, 104 (1891).

¹¹E. H. Griffiths, British Association Report, 1890; Ezer Griffiths, "Methods of Measuring Temperature," Charles Griffin and Company, Ltd., London, 1918, p. 51.

established, Callendar organized the available data and formulated a system which has remained in use until today.

Resistors

A simple resistance thermometer makes use of the principle of the Wheatstone bridge. Of the four resistance elements which are essential in such an arrangement, either one, two, or four¹² may be temperature-sensitive. Ideally, these units should vary in resistance only with temperature; the others, since they are used for purposes of comparison, should not vary in resistance under any conditions.

Good temperature-sensitive units should have the following general characteristics: (1) a known relationship between the temperature of the resistor and its resistance; (2) a high temperature coefficient of resistance; and (3) reliable constants which do not change with the history of the unit. In the measurement of small temperature differences, the second characteristic is the most important.

Temperature-sensitive resistors may be made from pure metals or from alloys. Platinum,¹³ copper,¹⁴ nickel,¹⁵ and alloys such as "Hytemco"¹⁶ and phosphor-bronze¹⁷ have been used. The coefficients, $d\ln R/dT$, of resistance elements made from these materials range from .004 to .006 deg.⁻¹.

Changes in temperature should have practically no effect on the resistance of the comparison units. In the early history of resistance thermometry, german silver and platinum-silver al-

¹²S. W. Watson and M. C. Henderson, Proc. Roy. Soc. (London), A118, 318 (1928).

¹³C. W. Siemens, op. cit., 1871.

¹⁴Charles G. Maier, J. Phys. Chem., 34, 2860 (1930); Loraine Decherd and Arnold Romberg, Phys. Rev., 39, 858 (1932).

¹⁵W. del Regno, Rend. Accad. Sci. Napoli, III 32, 194 (1926); W. H. Apthape, British Patent No. 271,296 (1926).

¹⁶J. S. Marsh, "Alloys of Iron and Nickel," McGraw-Hill, New York, 1939.

¹⁷J. F. Allen and E. S. Shire, Nature, 139, 878 (1937).

loys¹⁸ were used. More suitable alloys,¹⁹ such as manganin and constantan with values of $d\ln R/dT$ of approximately 10^{-6} deg.⁻¹ were later adopted. Recently, gold-chromium alloys²⁰ have been developed. The resistance, R , of such alloys may be represented by the following equation:

$$R_t = R_{25} [1 + \alpha (t - 25) + \beta (t - 25)^2]$$

For one such alloy, containing 2.1 per cent chromium, $\beta = 0$ between 20°C. and 30°C. and α may, by heat treatment, be made very small. In practice, less than 10^{-7} has been obtained. Moreover, the pressure coefficient of resistance for this alloy is only 1.1×10^{-6} atm.⁻¹. Because of these low coefficients, it is possible, by regulation of the temperature to 0.01°C. and by regulation of the pressure to one millimeter, to keep the resistance constant to about 1 part in 10^9 . This work therefore solves the problem of maintaining constancy of resistance in the temperature-insensitive units of the bridge so far as temperature and pressure effects are concerned.

Chemical change and mechanical strain are two other common causes of variation in resistance in both temperature-sensitive and temperature-insensitive units. Chemical change takes place gradually and though it is of significance for temperature measurement, it is not of importance for temperature difference measurement. Strains causing fluctuations in resistance may be due to mechanical defects in the mounting, which make the strain vary with small motions or vibrations of the unit, or they may be due to ill chosen insulators which change in dimensions with changes in humidity. The latter difficulty was studied by Dike;²¹ he found that an insulator composed of mixed pineapple and silk fibres (producing opposite effects on the resistance) was humidity-

¹⁸H. L. Callendar, op. cit., 1891.

¹⁹F. E. Smith, Phil. Mag. (6) 24, 541 (1912); Paul H. Dike, U. S. Patent No. 2,026,616 (1936).

²⁰J. O. Linde, Ann. Physik, 402, 52 (1931); 407, 219 (1932); J. L. Thomas, J. Res. Nat. Bur. Standards, 13, 681 (1934); Theodore B. Godfrey, J. Res. Nat. Bur. Standards, 22, 565 (1939).

²¹Paul H. Dike, op. cit., 1936.

insensitive. There is an abundant literature ²² on mountings designed to prevent strain in resistors and to insure good thermal contact of the temperature-sensitive resistors with their surroundings.

The Measurement of Resistance and Resistance Change

General methods for the precision measurement of resistance are (1) the potentiometer method,²³ (2) the Thompson or Kelvin double bridge method,²⁴ and (3) the Wheatstone bridge method.²⁵ Of these, the Wheatstone bridge method is the most widely used. A galvanometer is connected to the opposite corners of the bridge and the unknown resistance is measured either by (1) the deflection of the galvanometer or (2) the compensatory adjustment of one of the resistances in the bridge (the so-called nul method). The first method has not been used extensively. Descherd and Romberg²⁶ have, however, designed such a thermometer with two copper and two manganin arms in the bridge. Such an instrument is not suitable for high precision resistance measurements, though it can be used in some differential measurements. The nul method, in which the deflection of the galvanometer is brought to zero, is at present used in nearly all resistance measurements.

Evaluation of the Resistance Thermometer

As already stated, a single direct current resistance thermometer may be used to measure temperatures throughout an in-

²²W. H. Apton, British Patent No. 271,296 (1936); Siemens Brothers, Ltd., British Patent No. 276,464 (1926); The Cambridge Instrument Company, Ltd., British Patent No. 359,380 (1931); J. A. Hall, J. Sci. Instruments, 10, 4 (1932); C. H. Meyers, Bur. Standards J. Research, 9, 807 (1932); Clarence Johnson, Canadian Patent No. 358,928 (1936).

²³American Institute of Physics, "Temperature Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941, pp. 166, 265.

²⁴F. E. Smith, op. cit., 1912; J. A. Hall, Phil. Trans. (London), A229, 1 (1929-30).

²⁵F. E. Smith, op. cit., 1912; Marion Eppley, Rev. Sci. Instruments, 3, 687 (1932); E. F. Mueller, Bur. Standards Bulletin, 13, 547 (1935).

²⁶Lorraine Descherd and Arnold Romberg, Phys. Rev., 39, 858 (1932).

terval of 2000° , a range greater than that of any other precision thermometric device. The sensitivity (about 10^{-4} deg.) of this instrument is limited by that of the galvanometer employed, the difficulty of amplifying the direct current output of the Wheatstone bridge and the low temperature coefficient of resistance of metals. The sensitivity of a multijunction thermel can be of the order of 10^{-7} deg.²⁷ One of the most serious limitations to any thermometer is the conduction of heat²⁸ by metal wires entering the region whose temperature is to be measured. If a thermel and a resistance thermometer are both designed so as to have a sensitivity of 10^{-4} deg., the heat leakages are of the same order of magnitude. It is impossible, with thermoelectric materials now known, to increase the sensitivity without increasing the thermal leakage. If it should prove possible to increase the sensitivity of the resistance thermometer without a corresponding increase in the leakage, it would be possible to make measurements of higher precision than can now be made.

²⁷E. Lange and A. L. Robinson, op. cit.

²⁸Walter P. White, "The Modern Calorimeter," The Chemical Catalog Company, Inc., New York, 1928, p. 82.

PART II

AN EXPERIMENTAL INVESTIGATION OF THE POSSIBILITY OF MEASURING SMALL TEMPERATURE DIFFERENCES BY ALTERNATING CURRENT METHODS

Since the alternating current output voltage of an unbalanced Wheatstone bridge can be amplified, and can be detected with an electronic oscillograph; and since the temperature coefficient,²⁹ $d\ln R/dT$, of some solutions is about 0.05 as compared with 0.006 for the more sensitive metals, it should be possible to increase the temperature sensitivity of an impedance thermometer without a corresponding increase in thermal leakage.

Since a commercial oscillator of variable frequency, a 3-stage amplifier, a 15,000 ohm nickel resistor and an oscillograph³⁰ were all available, it was necessary to construct only three temperature-insensitive resistance units to make preliminary tests. These resistors were made of constantan wire No. 40 (B & S gauge) wound non-inductively (the direction was reversed for each adjacent layer and each layer had the same number of turns) on bakelite rod A and shielded by a copper shell S, Fig. 1.



Fig. 1.--Temperature-insensitive constantan resistor.
L = leads; A = bakelite rod; B = constantan wire; C = bakelite annular ring; S = copper shell.

²⁹S. Myamoto and Carl L. A. Schmidt, *J. Biol. Chem.*, **99**, 335 (1933); Carl L. A. Schmidt, "The Chemistry of Amino Acids and Proteins," C. C. Thomas, Baltimore, 1938, p. 672.

³⁰Built by Galen W. Ewing, cf. Ph. D. Dissertation, University of Chicago, 1939.

The assembled apparatus (Fig. 2) included an oscillator O, a transformer T, a bridge B with nearly equal arms, an amplifier A, and an oscillograph E. The three temperature-insensitive resistors, R_1 , R_2 , and R_3 , together with the transformer T and the condenser C_1 were mounted in a large copper box which served as a shield against electrical interference. R_3 consisted of a fixed resistor (constructed like R_1 and R_2 but having a slightly smaller resistance) in series with a much smaller variable resistance.

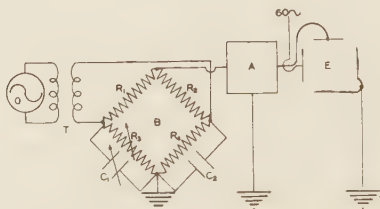


Fig. 2.--A diagram of assembled apparatus. O = oscillator; T = transformer; B = bridge consisting of R_1 , R_2 , R_3 , and R_4 (about 15,000 ohms each) and the capacities C_1 and C_2 ; A = amplifier; E = oscillograph.

A shielded, two-conductor cable led from the copper box to the temperature-sensitive nickel resistor, R_4 , located in a Dewar flask fitted with a stirrer so that the change in temperature could be controlled and followed with a Beckmann thermometer. Although there was some lag in R_4 , a good idea of the sensitivity was obtained as follows: While the temperature of the water in the Dewar flask was slowly dropping, simultaneous readings of the Beckmann thermometer and of the resistance were recorded. To balance the bridge, its output was fed into the vertical plates of the oscillograph E, Fig. 2. The amplitude of the signal was proportional to the applied voltage. At balance, the vertical amplitude approached zero and the signal was a horizontal line.

In such an apparatus, the temperature sensitivity, i.e., the smallest fraction of a degree detectable is determined by the temperature coefficient of resistance of the sensitive material and the precision with which the resistance can be measured. The resistance change is related to the output voltage of the bridge according to the formula

$$\delta E = E \delta R / 4R$$

where R is the resistance in one arm of the bridge, and δE is the change in its voltage output. Since $E/4R$ is practically constant, and since the voltage arising from lack of balance is linearly related to the amplitude of the signal, the sensitivity can be expressed as the temperature change corresponding to the smallest change in amplitude detectable on the oscillograph screen. This amplitude change happens to be about 1 mm., so that the sensitivity may be given in degrees per millimeter.

When the temperature was adjusted to produce perfect balance in the resistances of the bridge, the amplitude could be brought close to zero only if the frequency was adjusted to its optimum value (ca. 300 cycles/sec.). At any other frequency it was difficult to detect the variations in amplitude produced by temperature changes. This irreducible minimum was due to the lack of balance in the capacities and inductances resulting from the change in frequency. That is, the bridge was not balanced unless

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}$$

where the subscripts indicate any consecutive numbering of the impedances.³¹ The sensitivity was 10^{-3} deg./mm.

At this stage in the work the sensitivity of the apparatus was limited by the failure to obtain a good balance of the capacities and residual inductances of the resistors. This difficulty was reduced by replacement of all the resistors with better units (2,000 ohms), non-inductively wound and of very low capacity. In this arrangement there was no temperature-sensitive element in the circuit, but the objective at this point was only the development of the method of impedance measurement and the sensitivity was calculated from the smallest detectable impedance change of the variable resistances when the amplitude of the signal on the oscillograph was close to a minimum. As already stated, a millimeter change in amplitude was clearly discernible. The better resistors in the bridge made it possible to obtain a balance at maximum amplification and maximum output of the oscillator

³¹Leigh Page and Norman Adams, "Principles of Electricity," D. Van Nostrand Company, Inc., New York, 1931, p. 461.

(ca. 10 volts). However, a considerable amount of "noise," harmonics and sixty cycle hum, were evident. These made it difficult to estimate the sensitivity with accuracy.

The addition of an LC (inductance-capacity) tuning circuit, L and C_5 in Fig. 3 (a complete diagram of the amplifier used at that time), made it possible to eliminate a large part of these interfering frequencies, provided that the inductance L in the tuning circuit was properly placed and oriented. This

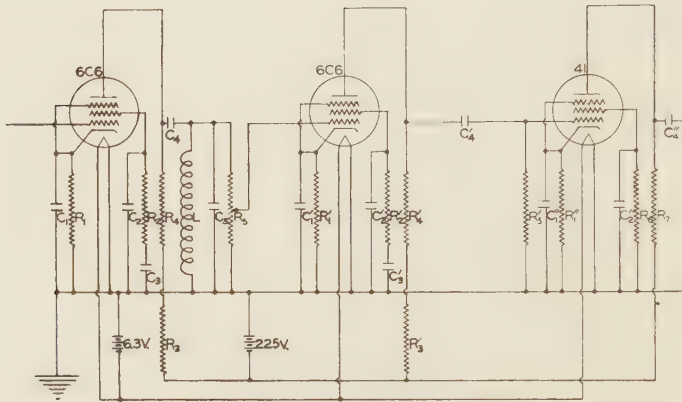


Fig. 3.--Amplifier with LC tuning circuit. $R_1 = 1300$ ohms; $R_2 = 1.5$ meg.; $R_3 = 50,000$ ohms; $R_4 = 0.25$ meg.; $R_5 = 1.5$ meg.; $R_6 = 1.5$ meg.; $R_7 = 0.3$ meg.; $C_1 = 10$ mfd.; $C_2 = 1$ mfd.; $C_3 = 1$ mfd.; $C_4 = 0.01$ mfd.; $C_5 = 0.1$ mfd.; L = inductance in tuning circuit.

inductance was one side of a common commercial transformer; its value could be changed by variation of the number of laminations in the iron core. In spite of the LC tuning circuit, however, much 60 cycle pickup was still evident. This was almost completely eliminated by means of an iron pipe which enclosed the transformer and provided electromagnetic shielding.

The output voltage of the bridge was increased by the installation of a bridge-to-grid transformer (Thordarson, T1A50). This transformer and the tube of the first stage of the amplifier were enclosed together in one shielding case. It was possible to

measure the sensitivity of the apparatus so modified, and to calculate, on the basis of the temperature coefficient of the glycine solution, the fraction of a degree that should be thus detectable. A resistance change of 1 part in 10^6 (corresponding to a temperature change of 10^{-4} deg./mm.) could be detected. A diagram of the complete circuit is shown in Fig. 4.

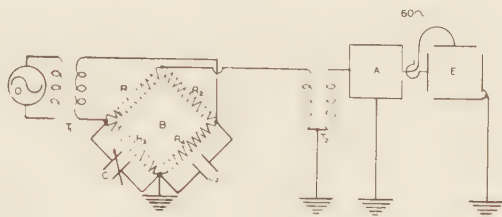


Fig. 4.--A diagram of assembled apparatus. O = oscillator; T_1 = audio transformer; B = bridge consisting of R_1 , R_2 , R_3 , R_4 (ca. 2,000 ohms each) and the small capacities C_1 and C_2 of a few micromicrofarads; T_2 , a bridge-to-grid transformer (Thordarson T1A50); A = amplifier; and E = oscillograph.

To verify the estimate thus obtained, cells were constructed to determine whether or not the bridge could be satisfactorily balanced with a glycine electrolytic cell in one arm. Several types of cells were tried. An account of a few of these follows.

The first cell, Fig. 5, was a large pyrex vessel made for other purposes, and was silvered by the method of Strong³² up to the level T, Fig. 5. Because the electrodes of the cell were large, and because the specific conductance of the (unpurified) glycine was high, the resistance of the cell was approximately equal to that of the other arms of the bridge. Little difficulty was experienced in obtaining a fairly good balance. The steadiness of the resistance showed the cell to be so large that it was not significantly affected by the fluctuations of the bath temperature ($\pm 0.01^\circ\text{C}$). It was necessary to fill the cell up to the

³²John D. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, 1931, p. 461.

constriction so as to avoid instability due to fluctuations in the position of the liquid surface.

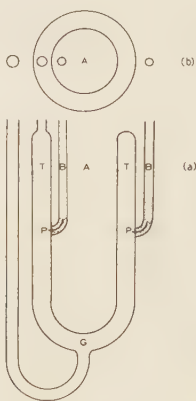


Fig. 5.--Glycine cell. (a) Longitudinal section; (b) transverse section. A = empty space; G = glycine solution; P = platinum wires; B = mercury; T = upper limit of silver coat.

A second cell was then constructed small enough to be immersed in a calorimeter where the temperature fluctuations were much smaller. This cell is shown in Fig. 6. Several materials for electrodes and leads were tried. Copper (attacked by glycine), copper with silver plating, silver, and nickel were used as electrodes; platinum and tungsten wires were used as leads. The cell shown in Fig. 6 consisted of two nickel electrodes spot-welded to tungsten supporting wires and sealed in a pyrex glass envelope. When difficulty was encountered in obtaining a balance in the bridge, poor contact resulting from tungsten oxide (possibly causing rectification) between the mercury and tungsten (C and S, Fig. 6) was suspected. The difficulty vanished when a small piece of platinum was spot-welded to each tungsten electrode.

After this demonstration that a balance could be obtained in a bridge with a glycine cell as an element, the task of increasing the sensitivity of the apparatus was again undertaken. This objective was accomplished by (1) elimination of hum in the

apparatus, (2) further amplification of the bridge signal and (3) an increase of the exactness of balance in the bridge.

Hum in the apparatus was greatly reduced by the elimination of all 60 cycle power supplied to the amplifier and the oscillator and by the removal of the oscillograph to a distance of about eight feet from the other parts of the apparatus.



Fig. 6.--An electrolytic cell. A,B = metal electrodes; G = glycine solution; S = tungsten supports; C = mercury.

Further amplification was realized by the replacement of the 41 tube by a 6C6 tube in stage three of the amplifier (Fig. 3) and by the addition of a regenerative tuning circuit in the second stage. This circuit is discussed further in connection with improvement of the bridge balance.

The greatest difficulty in balancing the bridge arises from the fact that it is impossible to construct a resistor free from capacity and inductance. It is necessary to consider contributions of these to the impedance. The two conditions under which a bridge is balanced, i.e., under which no current flows through the diagonal of the bridge are (1) that the resistances, capacities and inductances are separately and individually balanced or (2) that the impedance only is balanced and that the bridge current is strictly of one frequency, i.e., "monochromatic." It is almost impossible to meet either one of these two conditions exactly but if both conditions are approached closely, a balance good enough for practical purposes is obtained. It must be kept in mind that the balance of the bridge is affected also by conditions in other parts of the circuit. For example, the inductance and capacity to ground of the secondary winding on either side of the center tap of the plate-to-bridge transformer (T_1 , Fig. 4)

should be equal. An effort was made to obtain a transformer in which this ideal was closely approximated. The transformer finally selected required that a capacity of 400 micromicrofarads be included in C_1 of Fig. 4. In order to use the resistors with the low capacities and inductances and to make other improvements, a new bridge was constructed. This new bridge was supported on a bakelite frame and consisted of manganin resistors, non-inductively wound and having very little capacity. They were grouped close together to reduce loop inductance and placed away from sources of heat to avoid changes in resistance. The resistance of each arm of the bridge (Fig. 7) was a 2,000 ohm (shallcross)³³ resistor.

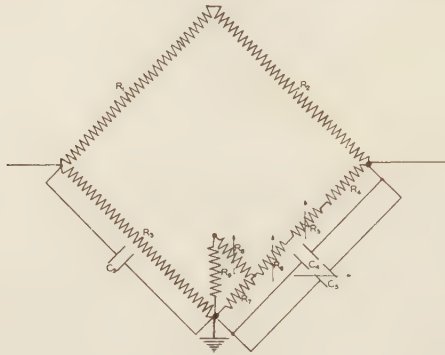


Fig. 7.--Impedance bridge. $R_1, R_2 = 2000$ ohms each; $R_3 = 1890$ ohms at $25^\circ\text{C}.$; $R_4 = 1000$ ohms; $R_5 = 1000$ ohms; $R_6 = 10$ ohms; $R_7 = 1$ ohm; $R_8 = 25$ ohms; $R_9 = 100$ ohms; $C_3 = \text{ca. } 0.01$ mfd.; $C_4 = 0.0095$ mfd.; $C_5 = 450$ micromicrofarads.

A part of one arm, R_4 , Fig. 4, consisted of a system of variable resistors of good quality. They made up only a very small fraction (11 ohms) of the total resistance in this arm. A 450 micromicrofarad variable condenser was used to balance the 400 micromicrofarad capacity of the transformer and certain other small capacities in the circuit.

To obtain the "monochromatic" frequency was a somewhat difficult problem. In the beat frequency commercial oscillator, there was not only a troublesome fluctuation, but also a misleading drift. The next step was to build a constant frequency feed-

³³Shallcross Manufacturing Co., Collingdale, Pa.

back oscillator designed in accordance with the recommendations of F. B. Lewellyn³⁴ who worked out mathematically the dependence of frequency on the various components of an oscillator. He showed that fluctuation in the voltage applied to an oscillator is the most serious drawback to constant frequency output. This voltage variation causes changes in the plate resistance (R_3 , Fig. 8), but these may be rendered unimportant by a much larger resistance (R_4 , R_5) in series. This oscillator (Fig. 8) produces

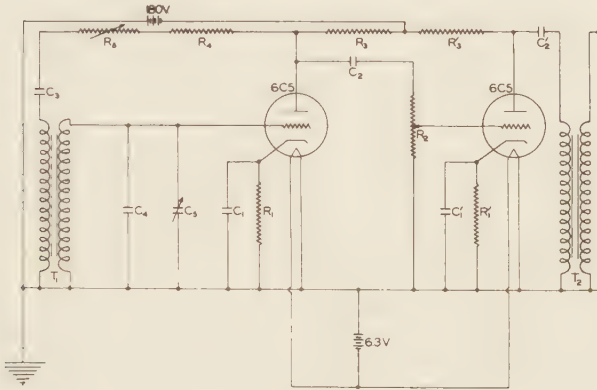


Fig. 8.--Constant frequency oscillator. $R_1 = 3450$ ohms; $R_2 = 500,000$ ohms; $R_3 = 50,000$ ohms; $R_4 = 6$ meg.; $R_5 = 2$ meg.; $C_1 = 25$ mfd.; $C_2 = 0.1$ mfd.; $C_3 = 0.1$ mfd.; $C_4 = 0.001$ mfd.; $C_5 = 250$ micromicrofarads; T_1 and T_2 are feedback transformer and output transformer, respectively.

very constant frequencies which can be adjusted to any value between 425 and 490 cycles/sec. The best frequency to use is one which (1) is farthest away from any harmonic of 60 cycles/sec., i.e., is $60n + 30$ cycles/sec.; (2) avoids excessive transformer losses, i.e., is less than 500 cycles/sec.; and (3) is high enough to avoid polarization effects. The frequency best satisfying these conditions is 450 cycles/sec. It is impossible completely to prevent the production of harmonics, but certain precautions were taken to reduce them to a minimum as follows: (1) Provision was made to regulate the feedback (by means of the variable resistor, R_5 , Fig. 8) so that just enough energy would be available for oscillation; (2) the resistance of the cathode was carefully

³⁴F. B. Lewellyn, Proceedings of the Institute of Radio Engineers, 19, 2063 (1931).

chosen;³⁵ (3) the impedances on both sides of the output transformer were selected so that they had the same ratio as the transformer impedances; and (4) a "high fidelity" output transformer was used.

However, the harmonics reaching the oscillograph were not sufficiently reduced by these measures. Further reduction was achieved by modification of the amplifier. A 6C6 pentode was installed at the third stage of the amplifier and instead of the LC tuning circuit at the second stage, a regenerative tuning circuit (C_7 , R_6 , R_7 , L_1 , L_2 , C_5 and C_6 in Fig. 9) was incorporated

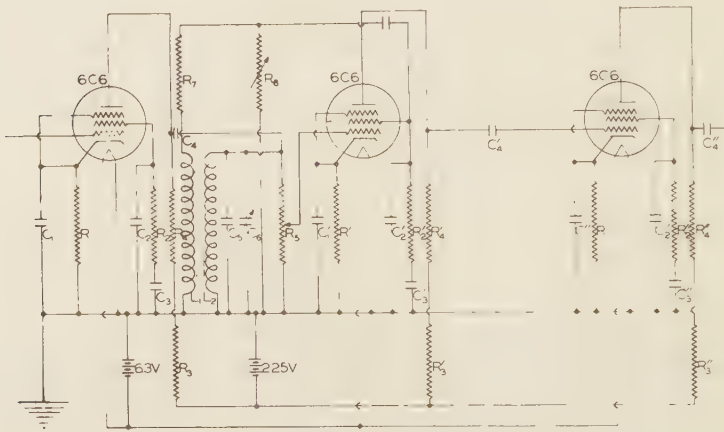


Fig. 9.--Amplifier with regenerative tuning circuit.
 $R_1 = 1300$ ohms; $R_2 = 1.5$ meg.; $R_3 = 50,000$ ohms; $R_4 = 0.25$ meg.; $R_5 = 1.5$ meg.; $R_6 = 50,000$ ohms; $R_7 = 50,000$ ohms; $C_1 = 10$ mfd.; $C_2 = 1$ mfd.; $C_3 = 1$ mfd.; $C_4 = 0.01$ mfd.; $C_5 = 365$ micromicrofarads; $C_7 = 1$ mfd.; L_1 , L_2 are transformer inductances.

by the use of a Thordarson 17A43 "high fidelity transformer." This latter tuning circuit, because it permits only the fundamental frequency to pass, increases the voltage of this funda-

³⁵RCA Manufacturing Company, "RCA Tube Manual," RCA Manufacturing Company, Harrison, N. J., 1937; Frederick E. Terman, "Radio Engineering," McGraw-Hill Book Co., 1937, p. 349.

mental frequency but leaves the other frequencies unchanged.

After these improvements had been made, it was found that a change in impedance of 5 parts in 10^8 could be detected. Such sensitivity is not attained without difficulty because the stability of the instrument is not good at such high amplification.

If it is possible to balance the bridge as successfully with two temperature-sensitive resistances (e.g., copper and nickel), as with the temperature-insensitive units, 5×10^{-6} deg./mm. could be detected. Under these same conditions a glycine cell should permit the detection of a temperature difference of 5×10^{-7} deg./mm. In order to determine what could actually be done with these temperature-sensitive resistors, copper and then nickel units (Fig. 10) were wound non-inductively on commercial



Fig. 10.--Metallic temperature-sensitive resistor (ca. 2000 ohms). L = manganin leads; E = bakelite cylinder; C = naphthalene; A = commercial form for resistor; D = bakelite disc; B = copper or nickel wire.

forms and fitted into brass cylindrical shells milled to fit closely over them. The small space remaining inside the shell was filled with naphthalene which increases the thermal conductivity without appreciably diminishing the electrical insulation. The shell was then mounted on a bakelite post suspended from the cover of a calorimeter and the copper resistor (temperature coefficient $0.41\% \text{ deg.}^{-1}$) connected as one arm of the bridge. The calorimeter, containing this resistor, one end of a thermel, a heater, and a cooling device, was placed in a 25°C . thermostated bath. Comparison of the resistance changes with the temperature variations indicated by simultaneous thermoelectric measurements

showed a linear relationship between resistance and temperature over an interval of 0.5°C . (Fig. 11). Since the electromotive

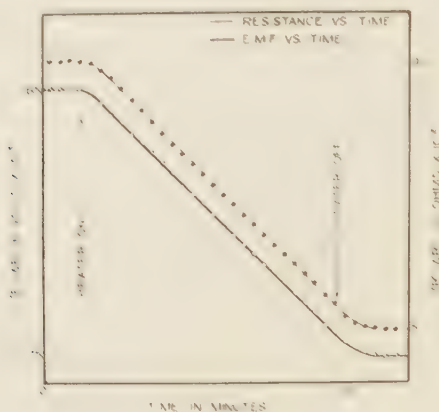


Fig. 11.--Plot of the simultaneous variations with temperature of electromotive force from a thermel and resistance in a temperature-sensitive resistor. E is an arbitrary electromotive force depending on the relative temperatures of the bath and calorimeter; R' is a small compensating resistance.

force of a thermocouple is a linear function of the temperature difference, the assumption of a linear relationship between resistance and temperature over this short range is justified. The nickel resistor, constructed and mounted in the same way, gave similar results. A sensitivity of about 10^{-6} deg. mm. was observed.

A glycine cell (Fig. 12) was next made from a conventional platinum in quartz conductivity cell. To increase the temperature coefficient of resistance, the amount of electrolytic impurity was reduced by recrystallization of the glycine first from water and then from water-alcohol solutions.³⁶ The apparatus was adjusted so that the glycine cell showed a sensitivity of 5×10^{-6} deg. mm. deflection. Because of the high capacity of this cell, the balance obtained was not as good as that obtained with the metallic

³⁶ An alternative method of reducing the amount of electrolytic impurity is recrystallization from glycerine-water mixtures as described by Beilstein, Band IV, S. 336.

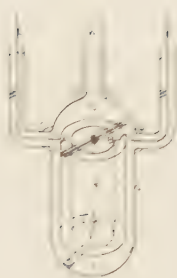


Fig. 12.--Electrolytic cell. Q = quartz envelope; A, B = platinum concentric electrodes; D = quartz supports for electrodes sealed to quartz envelope; F = platinum wire attachment for quartz supports; G = glycine solution; L = platinum leads; W = special paraffin wax; C = picene cement.

resistors. Hence, it was not possible to use the maximum sensitivity of the apparatus.

Conclusions

One of the objectives of this investigation was to develop a method for measuring small temperature differences produced in a micro-calorimeter. It has not been possible to develop a temperature sensitivity satisfactory for this purpose. However, a sensitivity in impedance measurement better than 1 part in 10^7 has been obtained, which seems to be the highest sensitivity reached thus far. This sensitivity makes possible many applications of the impedance thermometer. One other attractive feature of this method is that the heat leakage can be made very small. Thus, the method can be used for calorimeters which are well insulated from their surroundings and therefore unsuited to the use of thermals. This method is well adapted to the measurement of continuous heat processes such as those involved in biological reactions and in radioactive disintegrations. In certain instances the energy of light absorption may be measured by the impedance method. Many control devices depending on small changes in resistance operate on the bridge principle.³⁷ If direct currents are used in such regulators, a steady

³⁷C. J. Penther and D. J. Pompeo, Electronics, 14 (4), 20 (1941).

support for the current detecting device (galvanometer) is required. There are occasions when precise temperature measurements must be made under conditions where steady supports are not possible. Since the oscillograph does not require such supports, an alternating current method may be used.

A possible disadvantage of the impedance method is that heat is generated by the bridge current and if sufficiently large, may become a source of error. For the apparatus as constructed, the heat developed is 6×10^{-3} cal./sec. in one side of a differential calorimeter (containing two arms of the bridge) when a 10 volt potential is applied to the bridge, each of the four arms of which is about 2000 ohms. The heat of stirring³⁸ is 2.5×10^{-3} cal./deg. for a typical stirrer operating at 60 revolutions per minute. If heat is produced in either manner at a constant rate, no error results, provided that measurements are made after the calorimeter has come to thermal equilibrium. There is, however, an error caused by any departure from current constancy in the bridge arms, resulting from a change in resistance of the bridge units with change in temperature. The following calculation of the magnitude of this error shows it to be negligible for the apparatus as now constructed. If H calories are produced in a thermodynamic process, there will be a change in temperature of $10^{-3} H$ deg. in a calorimeter whose heat capacity is 1000 cal./deg. For a metal resistor with a temperature coefficient of resistance of 0.6 per cent per degree, this corresponds to a resistance change and therefore a change in rate of heat production of $6 \times 10^{-4} H$ per cent. On the basis of the total heat production of 6×10^{-3} cal./sec. in one side of the calorimeter, this would amount to $3.6 \times 10^{-8} H$ cal./sec. for the period during which this current inequality persists. The error produced during each minute of this period is thus only 2.16×10^{-4} per cent. The small magnitude of this effect may make possible the use of higher voltages across the bridge.

The sensitivity of the apparatus can probably be further increased by augmentation of the voltage input to the bridge, by

³⁸Walter P. White, *op. cit.*, p. 65; White, *J. Am. Chem. Soc.*, **40**, 1880 (1918); T. W. Richards and L. L. Burgess, *J. Am. Chem. Soc.*, **32**, 448 (1910); F. Barry, *J. Am. Chem. Soc.*, **44**, 911 (1922); C. E. Ronneberg, Ph. D. Dissertation, University of Chicago, 1935.

improvement of the bridge balance and by the production of higher amplification of the output signal from the bridge. The voltage input to the bridge may be augmented by raising the plate voltage of the oscillator. The balance may be improved by the addition of a degenerative tuning circuit to the amplifier system. This type of tuning device eliminates all frequencies except the fundamental one by feeding them back, in an even number of stages, out of phase. Additional improvement in balance may be realized if the capacities and inductances of the bridge resistors are further reduced. Since the "noise" level has not quite been reached, higher amplification is possible; this may be obtained by the addition of another amplifier stage or by an increase in the step-up ratio of the bridge-to-grid transformer. The stability of the apparatus may be improved by better shielding and by adequate cushioning of this apparatus against mechanical disturbances. After these improvements are made, it may be possible to use the impedance thermometer in micro-calorimetry.

Summary

The first part of this discussion describes the development, uses, advantages, and limitations of the direct current resistance thermometer; the second part is an account of an experimental development, by means of electronic devices, of an instrument using low frequency alternating currents in the measurement of changes in impedance with temperature. A change in impedance of 5 parts in 10^8 can be detected in a bridge circuit with nearly equal arms of low inductance and low capacity. Resistors constructed here permitted the detection of 10^{-5} deg./mm. to 5×10^{-6} deg./mm. deflection. This device is not at present useful for micro-calorimetry which requires a sensitivity of ca. 10^{-6} deg., but is suitable for other purposes. The error caused by the heating effect of the bridge current was shown, by calculation, to be negligible. Though the apparatus described has some advantages in its present stage of development, its chief advantage lies in the possibilities for its further development. Suggestions are given for making some of these improvements.

